
UNIVERSITI PUTRA MALAYSIA

# DEVELOPMENT OF AN ELECTRODE USING CARBON NANOTUBES AS A SUPPORT MATERIAL FOR DIRECT METHANOL FUEL CELL

RAMZIA ABDUL-MALIK SALEM.



# DEVELOPMENT OF AN ELECTRODE USING CARBON NANOTUBES AS A SUPPORT MATERIAL FOR DIRECT METHANOL FUEL CELL

By

RAMZIA ABDUL-MALIK SALEM

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in the Fulfilment of the Requirements for the Degree of Masters of Science

April 2006

**In the name of ALLAH, Most Gracious, Most Merciful**

**Dedication to**
**The memory of my beloved parents**
**To my beloved family**

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

**DEVELOPMENT OF AN ELECTRODE USING CARBON NANOTUBES AS A SUPPORT MATERIAL FOR DIRECT METHANOL FUEL CELL**

By

**RAMZIA ABDUL-MALIK SALEM**

**April 2006**

**Chairman:** **Syed Javaid Iqbal, PhD**

**Faculty:** **Engineering**

Global interest in renewable power sources to cut back the current fuel emission levels and to solve the foreseen fuel crisis makes the development of a new fuel cell system a necessity.

A fuel cell is an electrochemical device that produces electricity by separating the fuel (generally) hydrogen gas in the presence of a catalyst. Hydrogen Fuel cell is the simplest form of fuel cell but there are major problems with storing and transporting hydrogen due to high combustibility. Another alternative to Hydrogen FC is the Direct Methanol Fuel Cell (DMFC). The net energy density of methanol is higher than any other type of fuel (5.26kWhkg$^{-1}$). Hydrogen as a fuel has a net energy density of 0.2kWhkg$^{-1}$. Yet, there are two major problems associated with DMFC, firstly, the fuel anode reactions are much slower than the hydrogen fuel cell reaction, and secondly, methanol crossover through the membrane. To address the former, a catalyst must be used to accelerate the

reaction. It is now more or less a standard to use a mixture of Platinum and Ruthenium as the bimetallic catalyst. However the amount of loading, typically 4mg/cm$^2$ is too high and tampers the commercialization of the DMFC. This is solved by the use of a properly supported catalyst. Due to electrical conductivity and high surface area of Carbon, it is widely used as the support material. However, the amount of metal catalyst to support material, the loading per cm$^2$, and the form of carbon support to be used is not yet standardized. Lately, Carbon Nanotubes (CNTs) have attracted much attention due to their excellent electrical properties, surface inertness and large surface area.

CNTs have been synthesized using the Chemical Vapor Deposition (CVD) method. The synthesized CNTs were functionalized using 12M nitric acid, to activate their surfaces to enable anchoring the metal ions to them. Different ratios of catalyst/CNT were prepared by chemical reduction method of CNTs and metal precursors in a mixture with a reducing agent, ethylene glycol. The metal catalysts to CNT ratios were 40, 30 and 20 wt. % PtRu/CNT. The anodes were fabricated having different loadings ranging from 0.2 to 1.0 mg/cm2. The anodes were then characterized electrically via I-V curves and electrochemically using the cyclic voltammetry.

The anode design parameters were set to minimize the bimetallic catalyst loading to minimum without tampering the performance. The anode with the least metal to CNT ratio (20 wt.% PtRu/CNT) exhibited some very interesting results. The electrochemical activity of that particular anode with loadings of 0.2 mg/cm$^2$ and 0.4 mg/cm$^2$ was the highest among the other two (30 wt.% and 40 wt% PtRu/CNT). It was also found that, as the loading anode increases, the electro catalytic activity decreases. This is because

the Pt catalyst is not being accessible to both the electrical and the ionic conductors. Hence, the catalyst layer has to be as thin as to be in contact with both sides of the cell, yet loading has to be enough to be able to oxidize the methanol. In this project, anodes were fabricated and characterized to give the highest electro catalytic activity with the least precious metal loading.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

**PEMBANGUNAN SISTEM BAHANAPI SEL OLEH ELEKTROD MENGGUNAKAN NANOTIUB KARBON SEBAGAI BAHAN PEMANGKIN UNTUK SEL BAHANAPI METANOL LANGSUNG**

Oleh

**RAMZIA ABDUL-MALIK SALEM**

**April 2006**

**Pengerusi:** **Syed Javaid Iqbal, PhD**

**Fakulti:** **Kejuruteraan**

Kecenderungan global masa kini terhadap sumber-sumber tenaga boleh diperbaharui untuk mengurangkan tahap mengeluaran gas merbahaya daripada pembakaran bahanapi berasaskan petroleum dan mengurangkan penggantungan terhadap bahanapi petroleum menyebabkan pembangunan sistem sel bahanapi sesuatu yang mustahak.

Satu sel bahanapi adalah alat elektromagnetik yang dapat menghasilkan elektrik dengan mengasingkan bahanapi, biasanya, hidrogen dalam kehadiran pemangkin. Sel bahanapi hidrogen adalah yang sel bahanapi yang termudah, tetapi terdapat beberapa masalah terutamanya dari segi penyimpanan dan pengangkutan dalam kehadiran pemangkin disebabkan oleh sifat hidrogen yang mudah terbakar. Alternatif kepada sel bahanapi hidrogen ialah sel bahanapi metanol langsung (DMFC). Ketumpatan bersih tenaga metanol adalah lebih tinggi jika dibandingkan dengan sebarang bahanapi (5.25kWh/kg). Hidrogen sebagai bahanapi mempunyai ketumpatan bersih tenaga sebanyak (0.2

$kWhkg^{-1}$). Walau bagaimanapun ada dua masalah utama berkait dengan DMFC, iaitu yang pertama, tindak balas bahanapi di anod adalah lebih perlahan dibandingkan dengan sel bahanapi hidrogen, dan kedua, pergerakan berbalik methanol melalui membran. Untuk perbandingan dengan masalah pertama, suatu pemangkin perlu digunakan untuk mempercepatkan kadar tindak balas. Pada masa kini, ia menjadi amalan biasa untuk menggunakan campuran platinum dan ruthenium sebagai pemangkin dwilogam. Tetapi jumlah yang diperlukan, iaitu sebanyak 4 $mg/cm^2$adalah terlalu tinggi dan membantut usaha pengkomersilan DMFC. Untuk mengatasi masalah ini, pemangkin disokong di atas permukaan yang sesuai untuk meningkatkan keluasan permukaan. Karbon menjadi pilihan utama sebagai bahan penyokong kerana kondukvitinya yang baik dan keluasan permukaan yang tinggi. Nisbah pemangkin logam kepada bahan penyokong, muatan per $cm^2$ dan jenis karbon yang perlu digunakan belum di piawaikan. Kebelakangan ini nanotiub karbon (CNT) telah mendapat perhatian yang luas kerana sifat elektriknya yang baik, keluasan permukaan yang tinggi dan kelengaiannya.

CNT telah disintisiskan dengan menggunakan kaedah pemendakan wap kimia (CVD). CNT yang disintisiskan telah diaktifkan menggunakan 12 M asid nitrik, untuk mengaktifkan permukaan supaya dapat menyerap ion-ion logam. Pelbagai campuran dengan nisbah pemangkin/CNT telah disediakan melalui kaedah penurunan kimia menggunakan ajen penurunan, ethelen glikol. Nisbah pemangkin kepada CNT adalah 40, 30, 20 wt% PtRu/CNT. Anod dihasilkan mempunyai julat muatan dari 0.2 ke 1.0 $mg/cm^2$. Anod itu kemudiannya dicirikan menggunakan lengkuk I-V dan secara elektrokimia menggunakan voltammetri siklik.

Parameter rekabentuk anod telah dilaraskan untuk mengurangkan muatan pemangkin logam tanpa menjejas pretasinya. Anod dengan nisbah logam ke CNT (20 wt.% PtRu/CNT) telah memperlihatkan keputusan yang memberangsangkan. Aktiviti elektrokimia anod ini dengan muatan 0.2 $mg/cm^2$ dan 0.4 $mg/cm^2$ adalah tertinggi dibandingkan dengan yang lain. Juga didapati bahawa, apabila muatan anod meningkat aktiviti elektrod pemangkin akan berkurangan.

## ACKNOWLEDGEMENTS

First and foremost, it is with the help of God that this Master thesis project was possible and accomplished.

I consider myself one of the lucky ones whom had parents and family who from the start had done everything to motivate, support and guide me to set the goals and strive to achieve them. Both have stressed the importance of hard work, education, regimented discipline, and constant and never ending improvement. Without their endless love and support, I would not have been able to go on.

I would like to thank my supervisor, Dr. Syed Javaid Iqbal, for his moral support especially during the week of finalizing my thesis. I would also like to express my deepest gratitude to Assoc.Prof. Dr. Fakhru'l Razi Ahmadun who has given me the privilege to work in his lab in the Chemical Engineering to produce Carbon Nanotubes. I also would like to extend my gratitude to Dr. Mutaz Ali who has helped me and guided in the CNT production and made this thesis come true. My sincere thanks to Mr. Rahman Wagiran for all his helpful comments and advice throughout the course of my studies.

Last but not least, my special thanks and gratitude extended to my office back home, especially to my boss, whom I can't thank enough, Mr. Kousay Nadeem whom has been my mentor and guidance throughout the duration of my work and after and whom has dosed me with all the encouragement and support to continue with my higher studies.

I certify that an Examination Committee has met on 12th April 2006 to conduct the final examination of Ramzia Abdul-Malik Salem on her Master of Science thesis entitled "Development of an Electrode using Carbon Nanotubes as a Support Material For Direct Methanol Fuel Cell" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

**Samsul Bahari Mohd. Noor, PhD**
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

**Norhisam Misron, PhD**
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

**Hashim Hizam, PhD**
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

**Ibrahim A. Tallib, PhD**
Professor
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
(External Examiner)

**HASANAH MOHD. GHAZALI, PhD**
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

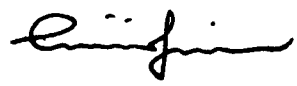
Date: 18 MAY 2006

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

**Syed Javaid Iqbal, PhD**
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

**Fakhru'l Razi Ahmadun, PhD**
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Member)

**Rahman Wagiran**
Lecturer
Faculty of Engineering
Universiti Putra Malaysia
(Member)



**AINI IDERIS, PhD**
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 08 JUN 2006

## DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

**RAMZIA ABDULMALIK SALEM**

Date: 15 / 5 / 2006

## TABLE OF CONTENTS

## LIST OF TABLES

## LIST OF FIGURES

## LIST OF ABBREVIATIONS

| | |
|---|---|
| DC | Direct Current |
| AFC | Alkaline Fuel Cell |
| DMFC | Direct Methanol Fuel Cell |
| PAFC | Phosphoric Acid Fuel Cell |
| MCFC | Molten Carbonate Fuel Cell |
| SOFC | Solid Oxide Fuel Cell |
| PEFC | Polymer Electrolyte Fuel Cell |
| PEMFC | Proton Exchange Membrane Fuel Cell/ Polymer Electrolyte Membrane Fuel Cell |
| MWCNT | Multi-Walled Carbon Nano Tube |
| SWCNT | Single-Walled Carbon Nano Tube |
| TEM | Transmission Electron Microscopy |
| SEM | Scanning Electron Microscopy |
| EDX | Energy Dispersive X-ray |
| A | Ammeter |
| V | Voltmeter |
| Pt | Platinum |
| Ru | Ruthenium |
| HRTEM | High Resolution Transmission Electron Microscopy |
| CVD | Chemical Vapor Deposition |
| EG | Ethylene Glycol |

| | |
|---|---|
| IPA | Isopropyl Alcohol |
| NBA | Normal Butyl Acetate |
| $CH_3OH$ | Methanol |
| M | Molar |
| keV | kilo electron Volt |
| RE | Reference Electrode |
| CE | Counter Electrode |
| WE | Working Electrode |
| CV | Cyclic Voltammetry |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background

The idea of a fuel cell is not a new one. In 1839, the first fuel cell was conceived by Sir William Robert Grove. In this cell a platinum electrode was immersed in nitric acid and a zinc electrode was immersed in zinc sulfate to generate 12 Amps of current at 1.8 volts. Grove invented a device such that the two ends of two platinum electrodes were immersed in a container of sulfuric acid and the other ends were sealed in containers of oxygen and hydrogen. By doing that he discovered that a constant current would flow between the electrodes. The sealed containers held water as well as hydrogen and oxygen. He noted that the water level rose in both tubes as the current flowed. Hence Grove's device produced water and electricity. However, this experiment did not produce enough electricity to be useful. In 1889, Charles Langer and Ludwig Mond tried to coin the term Fuel Cell by using air and coal gas [McDougall, 1976].

Not until 1932 that Francis Bacon developed the first successful fuel cell device with hydrogen – oxygen cell using alkaline electrolytes and nickel electrodes. However not until 1959 that Bacon first demonstrated a practical five-kilowatt fuel cell system.
During the 1960s, General Motors (GE) produced the first fuel-cell based electric power system for NASA's Gemini and Apollo space capsules. Today the space shuttle's

electricity is provided by fuel cells and the same fuel cells provide drinking water for the crew [Stroh, 2003; Kordesch and Simader, 1996].

### 1.1.1 What is a Fuel Cell

A fuel cell is an electrochemical device that converts the chemical energy of a fuel (hydrogen, natural gas, methanol, gasoline, etc.) and an oxidant (air or oxygen) into electricity. The reaction taking place only produces water and heat as its exhaust. Thus, it is very friendly to the environment.

In principle a fuel cell operates like a battery. However, a fuel cell does not run down or require recharging. It will produce electricity and heat as long as fuel and oxidizer are supplied. The most familiar electrochemical device used is the battery. In a battery there are two electrodes which are separated by an electrolyte. A battery has all of its chemicals stored inside and it converts those chemicals into electricity. This eventually means that the battery goes dead or has to be recharged. Generally, at least one of the electrodes is made of a solid metal. This metal is converted to another chemical compound during the production of electricity in the battery. The energy that the battery can produce in one cycle is limited by the amount of this solid metal that can be converted. In the fuel cell the solid metal is replaced by an electrode that is not consumed and a fuel that continuously refills the fuel cell. This fuel reacts with an oxidant such as oxygen from the other electrode. A fuel cell can produce electricity as long as more fuel oxidant is pumped through it.

### 1.1.2 How a fuel cell operates

The fuel cell is like an ordinary battery which provides DC electricity from two electrochemical reactions. These reactions occur at the electrodes to which the reactants are continuously fed. The negative electrode (anode) is being maintained by supplying a fuel such as hydrogen, whereas the positive electrode (cathode) is maintained by the supply of oxygen or air.

A fuel cell is an electrochemical device that produces electricity by separating the fuel (generally) hydrogen gas in the presence of a catalyst. The protons flow through a membrane (by diffusion) which is ion-conducting material. On the other side, in the presence of a catalyst, the hydrogen ions combine with oxygen to produce water. The electrons flow externally from the anode to the cathode where the electrons neutralize the H+, which is the source of electricity. As long as the hydrogen (fuel) and oxygen (air) are supplied to the fuel cell, electricity will always be produced. As shown in Figure 1.1, the hydrogen is supplied to the anode of the fuel cell and oxygen (from ambient air) enters the cathode. When a Hydrogen atom comes in contact with the catalyst, it splits into two H+ ions and two electrons ($e^-$). The electrons are conducted through the anode, where they make their way through the external circuit and return to the cathode side of the fuel cell. On the other hand, at the cathode side of the fuel cell, oxygen gas ($O_2$) is being forced through the catalyst where it forms two oxygen atoms. Each of these atoms has a strong negative charge. This negative charge attracts the two $H^+$ ions through the

membrane, where they combine with an oxygen atom and two of the electrons from the external circuit to form a water molecule ($H_2O$).

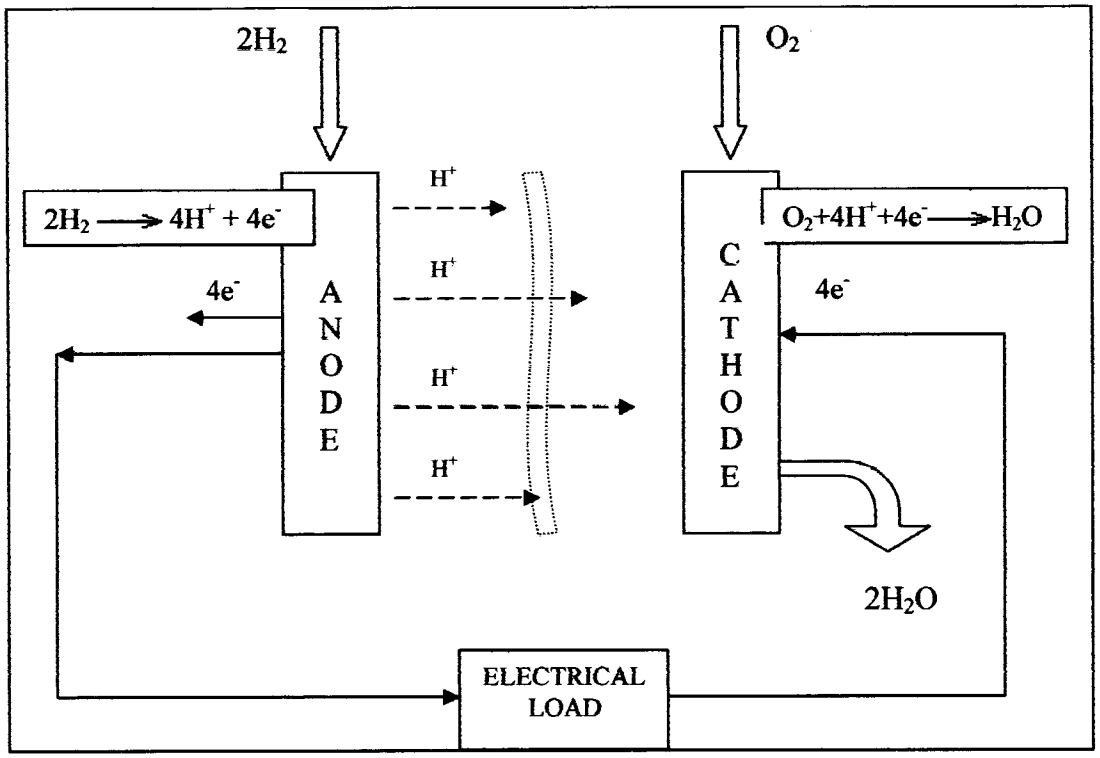



**Figure 1.1: A block diagram for a Hydrogen fuel cell**

The chemical reaction of the Hydrogen Fuel Cell is as follows:

At the anode side

$$2H_2 \longrightarrow 4H^+ + 4e^-$$

At the cathode side:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

The net reaction that takes place in the whole system is

$$2H_2 + O_2 \longrightarrow 2H_2O$$

### 1.1.3 Types of Fuel cells

There are several fuel cells developed so far since 1960 which are known as present era fuel cells: like, alkaline fuel cell (AFC), proton exchange membrane fuel cell (PEMFC), direct methanol fuel cell (DMFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), and solid oxide fuel cell (SOFC). Table 1.1 shows the basic types of fuel cells which are mainly classified by the electrolyte they are employing. Every cell has its own use and specificity which made its use limited or versatile. Among these, some are high temperature fuel cells as shown in Table 1.1. Hence, these are just limited to stationary use for power generation except PEMFC and DMFC which are low temperature fuel cell and have the potential to use for portable and mobile purposes similar to that what, now the battery is doing.

Types of fuel cells vary by the different materials used to make the electrolyte and the electrodes' catalyst.